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[71] Applicant:	Jiahu HUANG	Agent :	Jiawei PU
Address:	Huaxi Chemical Research Institute, West Chadianzi Street, Chengdu, Sichuan 610031		
[72] Inventor:	Jiahu HUANG		
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[54] Name of Invention:
A low-temperature desulfurizing agent that removes organic sulfur components from gases

[57] Abstract:
This invention is a desulfurizing agent that removes various kinds of organic sulfur components from gases. It is made up of a main agent (that contains at least two of the following: manganese dioxide, ferric oxide and zinc oxide), a supplementary agent (that contains at least one of the following: copper oxide and rare-earth metal oxides) and conventional fillers. Besides its sulfur removal ability, this desulfurizing agent is also capable of removing trace oxygen from gases.

CLAIMS

1. This is a kind of desulfurizing agent that is composed of metal oxides used for removing organic sulfur components from gases. It is characterized by its two kinds of components: a main agent (that contains at least two of the following: manganese dioxide, ferric oxide and zinc oxide), and a supplementary agent (that contains at least one of the following: copper oxide and rare-earth metal oxides). The composition (weight) of the main agent and the supplementary agent in the desulfurizing agent is 30 – 90% and 0.5% - 20% respectively, with the remaining part as the conventional fillers.

2. The desulfurizing agent, as described in (1) above, is characterized by its main agent that should contain manganese dioxide.

3. The desulfurizing agent, as described in (1) above, is characterized by its supplementary agent that should contain copper oxide.

SPECIFICATION

A Low-temperature Desulfurizing Agent that Removes Organic Sulfur Components from Gases

This invention is a desulfurizing agent that removes organic sulfur components from gases.

With the development of modern petrochemical technology, many high activity catalysts have stringent requirements in terms of sulfur content in feed gases (natural gas, synthesis gas, light gaseous hydrocarbon, light liquefied hydrocarbon gas, etc.). Generally some organic sulfur removal methods for such feed gases include oxidation, hydrogenation and hydrolysis, with the last two methods as the most common ones at present. The main existing problems with these desulfurizing agents are: (1) restricted applications and poor versatility, and (2) a higher desulfurizing activation temperature. For example, the Chinese patent CN85103555A presented an iron-manganese-zinc desulfurizing agent that though removes a wider range of organic sulfur compounds as compared to other similar kinds of desulfurizing agents, but is not applicable for gases that are unsuitable for hydrogenolysis and pyrolysis, the two main sulfur removal methods used by this desulfurizing agent. Furthermore, the activation temperature of the sulfur removal process is also higher, exceeding 350°C. Currently other catalysts for hydrolytic conversion do not only encounter the same lack of versatility in their applications, they also require other desulfurizing agents to remove its conversion product - hydrogen sulfide.

The first objective of this invention is to provide a desulfurizing agent that uses multiple conversion and absorption methods to remove organic sulfur components from gases, and that has good low-temperature activities.

The next objective lies in providing a desulfurizing agent that does not only possess the above-mentioned sulfur removal capability but is also able to remove trace oxygen from gases.

This desulfurizing agent is comprised of two components: a main agent and a supplementary agent. The main agent is made up of at least two of the following compounds: manganese dioxide, ferric oxide and zinc oxide; and the supplementary agent is made up of at least one of the following: copper oxide and rare-earth metal oxides. The rare-earth metal oxides in the supplementary agent can be the oxide of any rare-earth elements such as neodymium, lanthanum, thorium, cerium, etc., and can be better used as a rare-earth metal oxide mixture without separation and purification. The composition of the main agent and the supplementary agent in this desulfurizing agent is 30 – 90% (weight) and 0.5% - 20% (weight) respectively. The remaining part consists of conventional fillers, carriers (such as aluminum oxide, silicon oxide, graphite, clay, cement, etc.), lubricants, binders, etc. In order for this desulfurizing agent to simultaneously remove various kinds of organic sulfur components while removing trace oxygen from carbon monoxide and/or hydrogenous gases, it is recommended that, for the above-mentioned effective components, the main agent should contain manganese dioxide and/or the supplementary agent should contain copper oxide.

A significant feature of this invention is that, depending on the special characteristics and requirements of the gas, a single desulfurizing agent can be used to convert, absorb and remove different organic sulfur components (such as thiophene, mercaptan, thioether, carbonyl sulfide, disulfide, etc.) through cracking, hydrogenation, hydrolysis, etc. In addition it presents excellent low-temperature activities and sulfur capacity at breakthrough, and offers more options and a longer life span. For example, the activation temperature required to perform a fine desulfurization of organic sulfur components in light oil, natural gases, coke oven gas and hydrogen (total sulfur content may reach 500 – 1,000mgs/Nm^3) through hydrogenolysis and pyrolysis only needs to reach above 300°C. In comparison with other current similar desulfurizing agents, this is about 50°C lower. When hydrolysis is used to remove organic sulfur components from gases (such as coal gas, water gas, synthesis gas, conversion gas, etc.) that is rich in carbon monoxide, good transition and absorption activities can be achieved at 100°C and above. In comparison with other current similar desulfurizing agents, this is also about 50°C lower. Furthermore it offers more options and produces very little carbon monoxide disproportionation and methanation side reaction. When the desulfurizing agent, which contains at least manganese dioxide and/or copper oxide, is desulfurizing under an activation temperature it is also able to satisfactorily remove trace oxygen from the gas. For example, at a lower temperature between 100°C and 200°C, it can cause the trace oxygen to selectively combine with carbon monoxide to become carbon dioxide that will subsequently be removed; at a temperature between 150°C and 250°C, it can combine oxygen with hydrogen to form water that will subsequently be removed. The average removal rate of trace oxygen can reach above 80%, hence meeting the special requirement of some gases (e.g. synthesis gas for producing methanol) in having to remove sulfur and trace oxygen at the same time.

The following presents a few examples for this invention. Please refer to the following table for the composition (weight %) of each example. The various components can be industrial material and/or natural oxides or carbonates. They are evenly mixed before being formed into shape (using rolling depression, extrusion and pressing methods) and baked under conventional industrial methods to produce a desulfurizing agent that is ready for use.

Component / No.	**ZnO**	**MnO_2**	**Fe_2O_3**	**CuO**	**Rare-earth oxide compounds**	**Fillers**
1		45	5	2		Allowance
2	1	60	3	0.5		Allowance
3	55	4			5	Allowance
4	2	10	60	1		Allowance
5	60	5	2	12	0.1	Allowance
6	40	25	5		0.5	Allowance
7		5	65	1		Allowance
8		55	10	2	0.1	Allowance